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Synchronous fluorescence spectroscopic study of solvatochromic curcumin dye

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ABSTRACT

Curcumin, the main yellow bioactive component of turmeric, has recently acquired attention by chemists due its wide range of potential biological applications as an antioxidant, an anti-inflammatory, and an anti-carcinogenic agent. This molecule fluoresces weakly and poorly soluble in water. In this detailed study of curcumin in thirteen different solvents, both the absorption and fluorescence spectra of curcumin was found to be broad, however, a narrower and simple synchronous fluorescence spectrum of curcumin was obtained at $\Delta\lambda$ = 10–20 nm. Lippert–Mataga plot of curcumin in different solvents illustrated two sets of linearity which is consistent with the plot of Stokes' shift vs. the E_T30. When Stokes's shift in wavenumber scale was replaced by synchronous fluorescence maximum in nanometer scale, the solvent polarity dependency measured by λ_{SFS}^{max} vs. Lippert–Mataga plot or E_T30 values offered similar trends as measured via Stokes' shift for protic and aprotic solvents for curcumin. Better linear correlation of λ_{SFS}^{max} vs. π^* scale of solvent polarity was found compared to λ_{abs}^{max} or λ_{em}^{max} or Stokes' shift measurements. In Stokes' shift measurement both absorption/excitation as well as emission (fluorescence) spectra are required to compute the Stokes' shift in wavenumber scale, but measurement could be done in a very fast and simple way by taking a single scan of SFS avoiding calculation and obtain information about polarity of the solvent. Curcumin decay properties in all the solvents could be fitted well to a double-exponential decay function.

1. Introduction

Curcumin, 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione, is the main yellow bioactive component of turmeric (Curcuma longa), a perennial plant of the ginger family (Zingiberaceae), which is native to tropical South Asia [1]. It is extensively used as a spice, food preservative and coloring agent. It is a non-toxic, highly promising natural antioxidant compound having a wide range of biological applications. It is anticipated that curcumin may find applications as a novel drug in the near future to control various diseases, including inflammatory disorders, carcinogenesis and oxidative stress-induced pathogenesis [1–4]. Curcumin has drawn intense interest recently due to its potential pharmaceutical importance [5–16].

Curcumin has two aromatic rings with phenolic OH groups connected by an α,β-unsaturated-β-diketone (as given in Scheme 1). The β-diketone structure undergoes keto–enol tautomerism in solutions [17]. The relative contributions of the keto and enolic tautomers as well as their cis or trans form depend on factors such as solvent characteristics, temperature, polarity and substitution on curcumin [17–19]. However, at room temperature, the enolic form of diketones is in general predominant [19–21]. Curcumin absorbs in the visible region and gives fluorescence with low quantum yield. Emission properties highly depend on the polarity of its environment [17]. Its photochemistry, including reactions with oxygen, depends on the specific microenvironment of the molecule, such as polar or non-polar and protic or aprotic solvents. Curcumin is highly soluble in polar organic compounds but is slightly soluble in aliphatic or alicyclic organic solvents like hexane and cyclohexane.

In conventional fluorescence, an emission spectrum is obtained by scanning the emission monochromator at various emission wavelengths, λ_{em}, at a particular excitation wavelength, $\lambda_{ex,}$ and an excitation spectrum is obtained by scanning the excitation monochromator at various excitation wavelengths keeping the emission monochromator constant at a particular wavelength. The other possibility is to scan both the monochromators simultaneously, which is called synchronous fluorescence scan/spectroscopy (SFS). Synchronous fluorescence intensity (I_s) is directly related to the concentration of the analyte sample (c) as [22]

$$I_s = Kcb\,\mathrm{Ex}(\lambda_{ex})\,\mathrm{Em}(\lambda_{ex}+\Delta\lambda);$$
$$\text{or,}\quad I_s = Kcb\,\mathrm{Ex}(\lambda_{em}-\Delta\lambda)\,\mathrm{Em}(\lambda_{em});$$

where Ex is the excitation wave function at a given wavelength; Em is the emission wave function at a given wavelength; b is the thickness of the sample; K is the instrumental geometry and related parameters. SFS has been successfully used for various spectroscopic and spectrometric applications [23–27]. In this paper,

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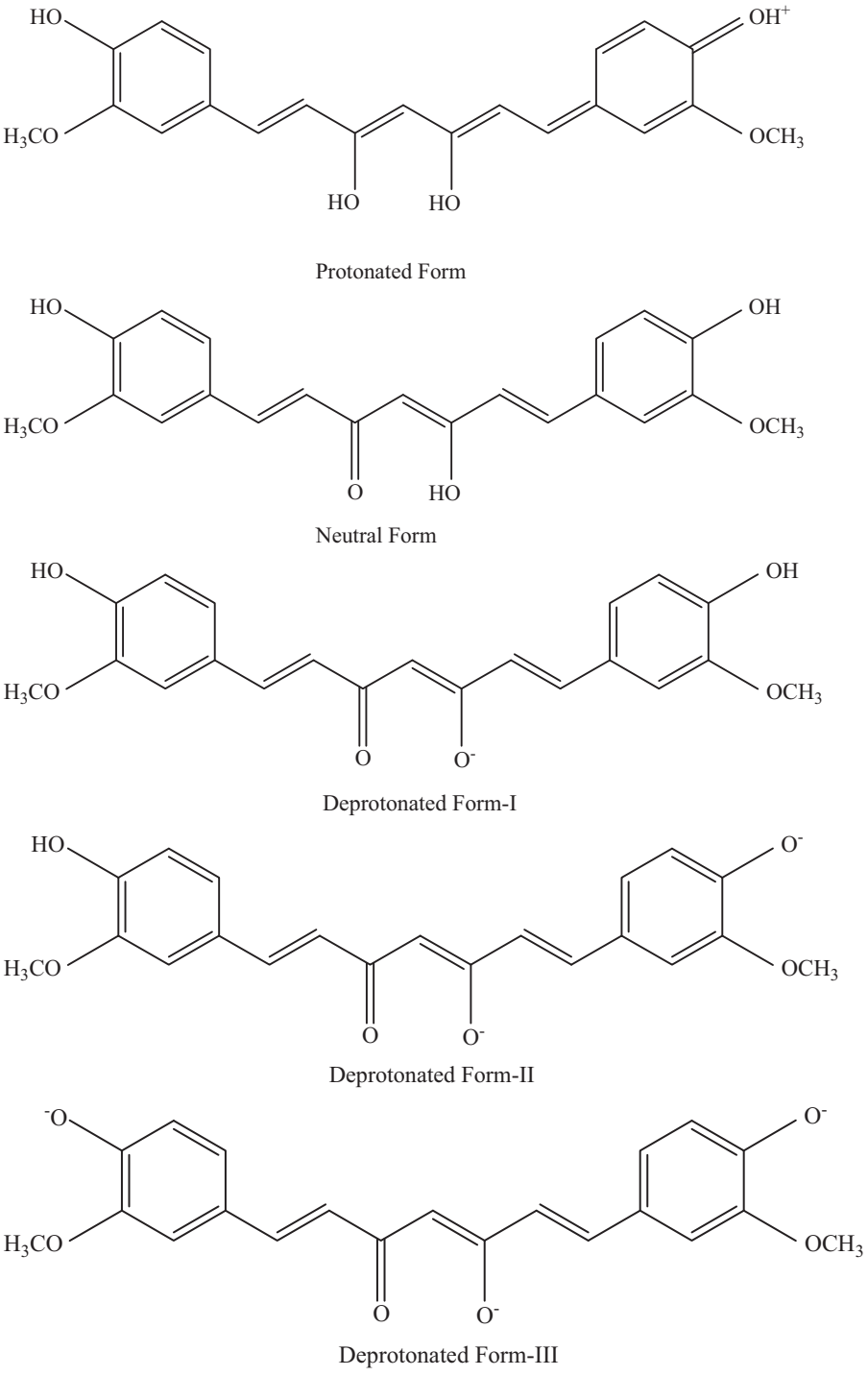

Scheme 1. Protonated, neutral and deprotonated form of curcumin.

the behavior of curcumin in different solvents is investigated in detailed by synchronous fluorescence spectroscopy and compared with conventional fluorescence measurements.

2. Materials and methods

2.1. Materials

Curcumin was obtained from Acros Organics and used without further purification. To prepare the stock solution, curcumin was dissolved in spectroscopic grade dichloromethane (Acros Organics). A desired amount of the stock sample was taken in a vial and the solvent, dichloromethane, was evaporated by gentle heating. Final sample solution was prepared by adding required amount of desired solvent into the same vial. Cyclohexane, ethanol, hexane, dichloromethane (DCM), 1,2-dichlorobenzene (DCB), 1,4-dioxane, tetrahydrofuran (THF), methanol, acetonitrile, n-butyronitrile (nBN), dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF) were of spectroscopy grade and obtained from Acros Organics. The solvents were used without further purification.